DOE/BC/15047-3
(OSTI ID: 14125)

IMPROVED EFFICIENCY OF MISCIBLE CO_2 FLOODS AND ENHANCED
PROSPECTS FOR CO_2 FLOODING HETEROGENEOUS RESERVOIRS

Quarterly Technical Progress Report
July 1, 1998-September 30, 1998

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Report Issue Date: October 21, 1998

Performed Under Contract No. DE-FG26-97BC15047

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Improved Efficiency of Miscible CO_2 Floods and Enhanced Prospects for CO_2 Flooding Heterogeneous Reservoirs

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ABSTRACT

In this quarter, we continued to test the horizontal-well capabilities of MASTER, the DOE's pseudomiscible reservoir simulator, by running simulation tests with several combinations of horizontal and vertical wells and various alternative reservoir descriptions. These sensitivity tests will be compared and validated using simulation results from a commercial simulator. This sensitivity study will be used in conjunction with our numerical tests on the comparison of foam injection processes and horizontal well injection processes. In addition, a preprocessor used to set up the input file to MASTER and a postprocessor for plotting the well performance were completed. Tests are in progress and the official version of MASTER will be released in the next few months.

We completed a series of foam coreflooding experiments in a composite core sample with two known regions of differing permeabilities. This composite core sample was used to demonstrate the effectiveness of foam in selective mobility reduction (SMR) and in improving oil recovery for a severe case where a high permeability contrast (permeability ratio of 1:10) is imposed between the two layers. Results indicate that "smart" foam will delay CO_2 breakthrough time, improve oil recovery efficiency, and correct nonuniform frontal displacement caused by the heterogeneity of the core samples.

We have started to look at sacrificial agents for foam application. We selected lignosulfonates as the first candidates and tested their foam properties using our foam durability apparatus at high pressure. We examined the compatibility of lignosulfonates with primary foam former Chase™ CD1045 and mixture properties. We found that lignosulfonates by themselves can form weak foam, usually lasting less than five minutes. Foam stability was affected by the amount of lignosulfonate added to surfactant CD1045. The stability of CD1045 foam was depressed at lignosulfonate concentrations higher than 7.5 wt%, while the stability of foam was somewhat affected at a moderate range of concentration (0.5 wt% to 5.0 wt%). These results will help in determining a reasonable concentration range when lignosulfonates are applied as a sacrificial agent with other primary foaming agents in foam flooding processes.

EXECUTIVE SUMMARY

A grant, "Improved Efficiency of Miscible CO_2 Floods and Enhanced Prospects for CO_2 Flooding Heterogeneous Reservoirs," DOE Contract No. DE-FG26-97BC15047, was awarded and started on June 1, 1997. This work examines three major areas in which CO_2 flooding can be improved: fluid and matrix interactions, conformance control/sweep efficiency, and reservoir simulation for improved oil recovery.

We continued testing in order to determine the horizontal-well capabilities of MASTER, DOE's pseudomiscible reservoir simulator. Sensitivity tests are used to compare with a commercial simulator. The sensitivity studies will be used in conjunction with our numerical tests on the comparison of foam injection processes and horizontal well injection processes. Additionally, a preprocessor setup for input to MASTER and a postprocessor for plotting the well performance have been completed. Tests are in progress and the official version of MASTER will be released shortly.

We completed a series of foam flooding experiments in composite core with two known regions of differing permeabilities. The composite core experiments demonstrate the effectiveness of foam in selective mobility reduction (SMR) and in improving oil recovery in a severe case where a high permeability contrast (permeability ratio of 1:10) is imposed between the two layers. Results indicate that "smart" foam will delay CO_2 breakthrough time, improving oil recovery efficiency, and correct nonuniform frontal displacement due to the heterogeneity of the core samples.

Our initial examination of lignosulfonates as sacrificial agents for foam application has shown some promise. An evaluation of the first candidate's foam properties using our foam durability apparatus at high pressures was completed and the compatibility of lignosulfonates with the primary foamer CD1045 and mixture properties was examined. We found that lignosulfonates by themselves can form weak foam, usually lasting less than five minutes. Foam stability was affected by the amount of lignosulfonate added to surfactant Chaser™ CD1045. The stability of CD1045 foam was significantly depressed at lignosulfonate concentrations higher than 7.5 wt%, while the effect was moderate at lower concentrations (0.5 wt% to 5.0 wt%). These results will help in determining a reasonable concentration range for lignosulfonates applied as sacrificial agents with other primary foaming agents in foam flooding processes.

INTRODUCTION

Because of the importance of CO_2 flooding to future oil recovery in New Mexico, west Texas, and the United States, the Petroleum Recovery Research Center (PRRC) pursues a vigorous research program to improve the effectiveness of CO_2 flooding in heterogeneous reservoirs. The results of our research continue to expand the list of viable candidates for CO_2 flooding. Our primary interest is to include more low-pressure reservoirs and many more heterogeneous or fractured reservoirs in our research.

Continued support for oil recovery research by CO_2 flooding has been provided by the U.S. Department of Energy for an additional three years through a grant entitled: "Improved Efficiency of Miscible CO_2 Floods and Enhanced Prospects for CO_2 Flooding Heterogeneous Reservoirs." The New Mexico Petroleum Recovery Research Center (PRRC) is well known as a premier institution for improved oil recovery (IOR) research and, in particular, for its research on the use of high-pressure CO_2 injection. The extension will continue the progress on understanding CO_2 flooding in heterogeneous reservoirs, further the development of methods to enable CO_2 flooding in more heterogeneous reservoirs, and continue the dissemination of this information to promote successful implementation of these methods. The research will proceed in three related areas:

- Fluid and matrix interactions (understanding the problems): interfacial tension (IFT), phase behavior, development of miscibility, capillary number (Nc), injectivity, wettability, gravity drainage, etc.

- Conformance control/sweep efficiency (solving the problems): reduction of mobility using foam, diversion by selective mobility reduction (SMR) using foam, improved injectivity, WAG, horizontal wells, etc.

- Reservoir simulation for improved oil recovery (predicting results): gravity drainage, SMR, CO_2/foam flooding, IFT, injectivity profile, horizontal wells, and naturally fractured reservoirs.

All areas originate from research on the mechanics of oil recovery by high-pressure CO_2. Experience gained during the current project is relevant to our continued efforts. Future research in each of the three areas will increase both the quantity of oil produced and the efficiency of oil

recovery from CO_2 flooding. Special attention will be given to disseminating research results through an extensive technology transfer effort. Because of the importance of CO_2 flooding in New Mexico reservoirs, additional funds are being provided through a combination of state and industry funds.

This report summarizes this quarter's study on assessing the technical feasibility of applying CO_2 flooding using horizontal wells, including an extended progress report on determining the effects of selective mobility control in zones without crossflow (with or without oil saturation) and on our development of sacrificial agents for improving the economics of foaming agents.

SUMMARY

Simulation. The primary motivation of our study was to assess the technical feasibility of using horizontal wells for CO_2 flooding. A reservoir simulator with horizontal well capabilities can provide guidance in the design of well lengths, locations, and other factors associated with horizontal wells. One of the objectives of this work is to conduct a systematic investigation of CO_2 flooding using horizontal wells in conjunction with foam. MASTER, a DOE pseudomiscible reservoir simulator which has been modified by incorporating the foam and horizontal-well features, is used in this investigation.

In this quarter, we continue to test MASTER's horizontal-well capabilities by running simulation tests with several combinations of horizontal and vertical wells and various alternative reservoir descriptions. These sensitivity tests will be compared and validated using simulation results from a commercial simulator. This sensitivity study will be used in conjunction with our numerical tests on the comparison of foam injection processes and horizontal well injection processes. In addition, a preprocessor used to set up the input file to MASTER and a postprocessor for plotting the well performance were completed. Tests are in progress and the official version of MASTER will be released in the next few months.

Mobility Control Tests. In this quarter, we completed a series of foam coreflooding experiments. The experiments were conducted in a composite core sample with two known regions of differing permeabilities. This composite core sample was used to demonstrate the effectiveness of foam in selective mobility reduction (SMR) and in improving oil recovery for a severe case where a high

permeability contrast (permeability ratio of 1:10) is imposed between the two layers. Our results indicated that in addition to delaying CO_2 breakthrough time and improving oil recovery efficiency, this "smart" foam is also useful in correcting nonuniform frontal displacement caused by the heterogeneity of the core samples.

We have started to look at sacrificial agents for foam application. We selected lignosulfonates as the first candidates and tested foam properties using our foam durability apparatus at high pressure. We examined the compatibility of lignosulfonates with primary foam former Chaser™ CD1045 and mixture properties and found that lignosulfonates by themselves can form weak foam, with stability usually lasting less than five minutes. Foam stability was affected by the amount of lignosulfonate added to surfactant Chaser™ CD1045. The stability of CD1045 foam was depressed at lignosulfonate concentrations higher than 7.5 wt%, while the stability of foam was slightly affected at a moderate range of concentration (0.5 wt% to 5.0 wt%). These results will help in determining a reasonable concentration range for lignosulfonates applied as a sacrificial agent with other primary foaming agents in foam flooding processes.

TECHNICAL PROGRESS

CO_2-Foam Core Flooding Experiments. A high-pressure coreflood apparatus was designed to conduct CO_2-foam experiments. The schematic diagram and a detailed description of this apparatus has been given in previous publications.[1,2] A noncommunicating-layered, composite core system with a large permeability contrast between the two layers (i.e., permeability ratio: 1:10) was prepared to test the foam in a fabricated heterogeneous environment. To prepare this core system, first a fired Berea core (6.7 cm long and 3.56 cm diameter) of 500 md permeability was epoxied and cast in a stainless steel sleeve. A 0.625 in. (1.6 cm) central hole was then drilled end-to-end and filled with relatively uniform (90-120 micron) glass beads. A summary of the core sample properties is given in Table 1.

A special dual outlet end cap was designed to collect the effluent fluid separately from the center and annulus sections of the composite core. The fluid inputs of the aqueous phase and of high pressure CO_2 entered the system from floating-piston-accumulators driven by distilled water, via a TEMCO injection pump and a Milton Roy pump. The input fluids were uniformly distributed to the inlet surfaces of the two different permeability regions. The output flows from the two regions were separated by a circular barrier of the same diameter as the central zone of the composite core. Each

of the two output regions have their own exit plumbing, each leading into a modified TEMCO BPR-50 backpressure regulator (BPR), in which the dome pressure was maintained at the test pressure (2100 psi). The two low pressure liquid outputs from the BPRs flow into receiving flasks, while the outputs of atmospheric pressure gas flow through a wet-test meter or a dry-gas meter for the volumetric measurements.

Tests were normally performed with a constant injection rate for either CO_2 alone, CO_2/brine (4:1 ratio) or CO_2/surfactant (4:1 ratio) at a typical Permian basin reservoir pressure and temperature (101°F and 2100 psig). Experiments were divided into two phases. In the first phase of experiments, the core sample was first saturated with either brine or surfactant solution prior to injection of CO_2. In the second phase of experiments, the core was saturated with crude oil to residual water saturation prior to CO_2 injection. The crude oil was filtered dead Sulimar Queen oil with a density of 0.83 g/cc and viscosity of 2.9 cp at the test condition of 101°F and 2100 psig. The brine was a synthetic solution with composition of 1.5 wt% NaCl and 0.5 wt% $CaCl_2$ in distilled water. In these tests the 2 wt% brine solution was used alone or with Chaser[TM] CD1045 surfactant at concentrations of either 500 ppm or 2500 ppm. Chaser[TM] CD1045 was identified as one of the best foaming agents in earlier studies.[3-5] All the tests were conducted at a constant injection rate for either CO_2 alone, CO_2/brine, or CO_2/surfactant with a volumetric ratio of 4 to 1. The CO_2 breakthrough time, and incremental recovery were recorded for each run. The properties of the aqueous fluids are shown in Table 2.

Experimental Description of Isolated Coaxial Core System. CO_2-foam experiments were conducted in an environment with a very large permeability contrast between the two isolated layers (permeability ratio of 10:1). The first set of experiments were run with no oil present. Prior to the injection of CO_2, the noncommunicating sample core was either saturated with brine or surfactant solution. In the second set of experiments, the core was saturated with the Sulimar Queen crude oil and displaced with either CO2, CO_2/brine, and CO_2/surfactant solution. When CO_2, CO_2/brine or CO_2/surfactant was injected into the core, the breakthrough time of CO_2 in each region was recorded. The brine and oil were collected in sample vials for 30-60 minutes during each displacement run. The effluent CO_2 was separated from the aqueous phase and volumetrically measured via a wet-test meter and a dry-gas meter. A summary of these runs is tabulated in Table 3.

Results and Discussion. We showed in our previous work[1,2,6] that CO_2-foam improves CO_2

breakthrough in composite cores with two permeability zones in capillary contact. In this study, the main objective is to examine the effectiveness of foam in improving oil recovery by diverting displacing fluid to the lower permeability region. In our experiments where no oil was present in the core (Table 3, run # 1, 2, 3, and 4), the unfavorable mobility ratio between CO_2 and the displaced fluid, enhanced by the heterogeneity of the core, caused CO_2 to channel through the higher permeability region. When CO_2 was used as the sole displacing fluid, CO_2 breakthrough occurred at 0.39 PV in the high permeability zone (center) and later, at 4.47 PV, in the low permeability zone (annulus). Coinjection of CO_2 and brine, simulating a quick and short cycle of WAG in the system, delayed CO_2 breakthrough to 0.82 PV in the high permeability region, but decreased time to breakthrough to 2.03 PV in the low permeability region. When surfactant was added to the brine, foam displacement delayed CO_2 production further in the high permeability region, but expedited production in the lower permeability section. In the high permeability region, CO_2 breakthrough occurred at the same time (0.89 PV) for both low and high surfactant concentrations. In the low permeability layer, CO_2 breakthrough occurred for the low and high surfactant concentration (Runs # 3 and 4) after about 1.37 PV and 1.16 PV fluid was injected, respectively.

CO_2 breakthrough behaved differently in experimental tests where oil was present. In the high permeability region, CO_2 breakthrough occurred earlier in all four runs (Runs #5-8 in Table 3) compared with tests in which no oil was present. At 500 ppm surfactant concentration, breakthrough did not occur in the low permeability region (Runs # 5-7 in Table 3) after about 2.78 PV, 5.16 PV, and 6.28 PV of CO_2, CO_2/brine, and CO_2/foam were injected, respectively. The CO_2 channeled through the high permeability zone and continued to flow preferentially, due to the high permeability contrast between the two layers. Only in the last experiment (Table 3, Run # 8), in which 2500 ppm surfactant concentration was used, was CO_2 breakthrough observed in the low permeability region. Here, CO_2 breakthrough occurred after about 3.32 PV of CO_2/foam was injected.

Figure 1 shows the fractional recovery of crude oil as a function of total pore volumes of displacing fluid injected. The recovery curves in this plot indicate the effectiveness of the displacing fluids in sweeping oil from the fully saturated high permeability section. These curves show that a water alternating gas (WAG) system works better than pure CO_2 injection. At higher surfactant concentrations, CO_2/foam shows better recovery efficiency. As indicated earlier, CO_2/foam at 500 ppm concentration could not divert the fluid into the lower permeability section and, as a result, no CO_2 breakthrough occurred after 6.28 PV injected.

Figure 2 depicts oil recovery from the low permeability section (annulus) as a function of total pore volume injected. This plot indicates that there was no oil production from the low permeability region for the first three runs where CO_2, CO_2/brine, and CO_2/foam at 500 ppm surfactant concentration were injected. Only the CO_2/foam test at 2500 ppm surfactant concentration was successful in the depletion of the low permeability section and a significant oil recovery. In this run, it appears that after the depletion of the high permeability section, foam started to form in the center section and gradually diverted the displacing fluid into the lower permeability layer (annulus) as the foam began to stabilize. The pressure profile for this experiment (see Figure 3) indicates how foam started to form about 125 minutes (2.4 PV) from the starting point. No production was observed during the first two hours of the test. However, oil production started as foam persisted to form in the high permeability region. Foam began to stabilize after about 300 minutes. The oil recovery curve in this plot follows the pressure drop profile. It indicates that, as foam became stronger, a larger fraction of the displacing fluid was diverted into the low permeability section and oil production was increased. This experiment clearly shows the effectiveness of foam in favorable mobility control, or SMR, in a very heterogeneous environment.

We will continue CO_2/foam experiments, but in a larger composite core sample in which we will be running tests on residual oil instead of residual water saturation. In these experiments, foam effectiveness will be tested in a system with a larger volume and in an environment where oil has been swept in some zones, allowing earlier foam production.

Sacrificial Agents for Foam Flooding

Foam Durability Experiment. The high-pressure foam durability test apparatus[7] was used to determine the properties of lignosulfonate, mixed surfactants (lignosulfonate with Chaser™ CD1045), and properties of foam generated by these surfactants. The apparatus consists of a CO_2 source tank, a visual cell made from a transparent sapphire tube, a buffer solution cylinder, and a Ruska pump. The major part of this system, the CO_2 tank and the sapphire tube high-pressure cell, is contained in a temperature controlled water bath. The buffer solution cylinder and the Ruska pump are installed outside the water bath, and their temperatures are maintained at the test temperature through another temperature control system.

During operation, the sapphire visual cell is first filled with the solution to be tested. Once the system is brought to the desired pressure by means of the Ruska pump, the dense CO_2 is introduced through a needle at the lower end of the cell. The CO_2 is drawn upward inside the cell

when the Ruska pump is in a withdrawing process. Because of the density difference between dense CO_2 and tested solution, CO_2 bubbles are formed and collected at the upper end of the cell. Depending on the effectiveness of the surfactant, these bubbles will then either form a layer of foam like dispersion at the top of the sapphire tube or coalesce into a clear layer of dense CO_2. After a standard volume of CO_2 (1.75 cc) has been introduced into the sapphire tube, the pump is stopped and the duration of formed foam is measured.

The lignosulfonate used in this study is Lignosite® 100 calcium lignosulfonate which was obtained from the Georgia-Pacific Corporation. This product is produced by sulfonation of softwood lignin and received in a powder form. Batch solution of lignosulfonate at concentration of 10 wt% was prepared by dissolving the product powders into a brine consisting of 1.5 wt% NaCl and 0.5 wt% $CaCl_2$. Lower concentration of lignosulfonate solution, ranging from 0.5 to 7.5 wt%, was prepared by dilution of the 10 wt% batch solution with a brine solution. The 10 wt% lignosulfonate solution has a pH value of 4.75 and a density of 1.069 gm/cc, while the surfactant solution, 0.05 wt% CD1045 has a pH value of 6.80 and a density of 1.020 gm/cc at room temperature compared to 1.013 for the brine. The screening tests on lignosulfonate solution and the mixture of surfactants were conducted at 77°F and 2000 psig.

Results and Discussion. Figure 4 presents the results of interfacial tension (IFT) between CO_2 and calcium lignosulfonate solution. The IFTs decrease with the surfactant concentration. The measurement was terminated at concentration of 10 wt%, as higher concentrations precluded bubble counting because of the dark-colored lignosulfonate solution. Figure 5 presents the results of static decay of the CO_2-foam using lignosulfonate as a foam former. The graph shows the percentage of the original foam volume remaining after the indicated time. This is an indication of the persistence of foam remaining inside the sapphire cell after a standard volume of CO_2 has been introduced. The . bubbles formed at lower lignosulfonate concentrations coalesced in less than a minute, whereas bubbles formed at higher concentrations lasted more than 5 minutes. At 7.5 wt% concentration, the CO_2-foam bubbles lasted about 20 minutes before fully coalescing. When 0.05 wt% surfactant CD1045 was mixed with lignosulfonate solution at different concentrations, the IFTs between dense CO_2 and the mixtures increased slightly as lignosulfonate concentration increased (see Figure 6). The results of static decay of CO_2-foam with mixtures indicate an opposite trend. The foam bubbles decay faster at higher lignosulfonate concentrations (above 7.5 wt%) and stabilize at concentration below 5 wt%. Some of the foam decay results are shown in Figure 7, where most of the foam

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bubbles remained intact for at least 90 minutes when less than 5 wt% of lignosulfonate was mixed with surfactant CD1045. Based on the static foam experimental results, we believe that lignosulfonates are compatible with surfactant CD1045 and are able to stabilize foam in static foam tests. In the following quarters, we will determine a reasonable lignosulfonate concentration range to be used when it is used as a sacrificial agent with surfactant CD1045, what adsorption preference there is between the components, and evaluate the mobility of foam with such a mixed surfactant system in porous media.

CONCLUSIONS

1. In composite core sample experiments, foam was effective in diverting displacing fluid from the high permeability region to the low permeability region and increasing oil recovery efficiency.

2. Lignosulfonate is a weak foaming agent, generating CO_2 foam bubbles at 2000 psig.

3. Lignosulfonate is compatible with surfactant Chaser™ CD1045 to stabilize foam bubbles in static foam durability tests.

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Table 1. Properties of isolated coaxial composite core								
Composite core sample	**Center Region**				**Annulus Region**			
	Type	**K (md)**	**φ**	**Area (cm²)**	**Type**	**K (md)**	**φ**	**Area (cm²)**
Isolated	Glass beads 90-120 μm	5000	0.42	1.27	Fired Berea sandstone	500	0.23	7.58
Length of the isolated coaxial core = 6.7 cm								

Table 2. Surfactant and brine properties					
Surfactant	Conc. (PPM)	pH	Type	Active (%)	Formula
Chaser™ CD1045	500	6.05	Anionic	46.7	(Not available) Manufactured by Chase International
	2500	5.88			
Brine	20000	5.75	----------	100	1.5 Wt % NaCl & 0.5 Wt % CaCl$_2$

Run #	Description	Q_t (cc/hr)/ (ft/d)	Ratio	Annulus		Center	
				Total PV Inj.	BT time (min)	Total PV Inj.	BT time (min)
1	CO_2 displaced brine	16.00/1.2	1	4.47	240	0.39	21
2	CO_2/brine displaced brine	16.45/1.3	4:1	2.03	109	0.82	44
3	CO_2-foam displaced surf. @500 ppm	16.45/1.3	1	1.37	74	0.89	48
4	CO_2-foam displaced surf. @2500 ppm	16.45/1.3	4:1	1.16	62	0.89	48
5	CO_2 displaced oil	16.00/1.2	4:1	2.78	N/A	0.26	14
6	CO_2/brine displaced oil	16.45/1.3	4:1	5.16	N/A	0.41	22
7	CO_2-foam displaced oil @500 ppm	16.45/1.3	4:1	6.28	N/A	0.41	22
8	CO_2-foam displaced oil @2500 ppm	16.45/1.3	4:1	3.32	178	0.47	25

Table 3. Summary of isolated coaxial composite core experiments

N/A: no breakthrough was observed
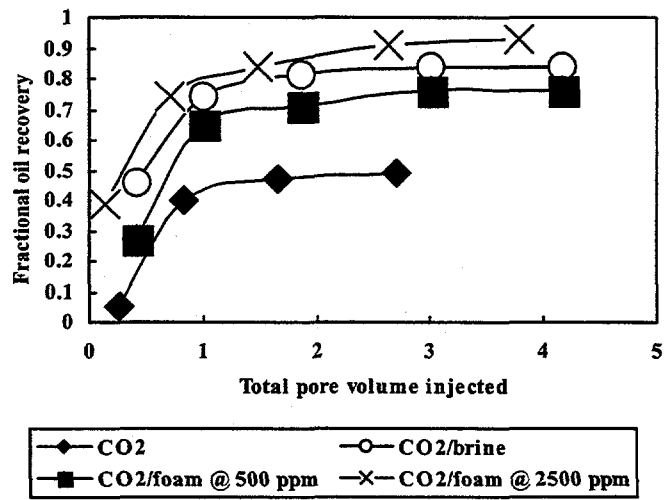
Figure 1. Oil recovery through the high permeability (center) region.
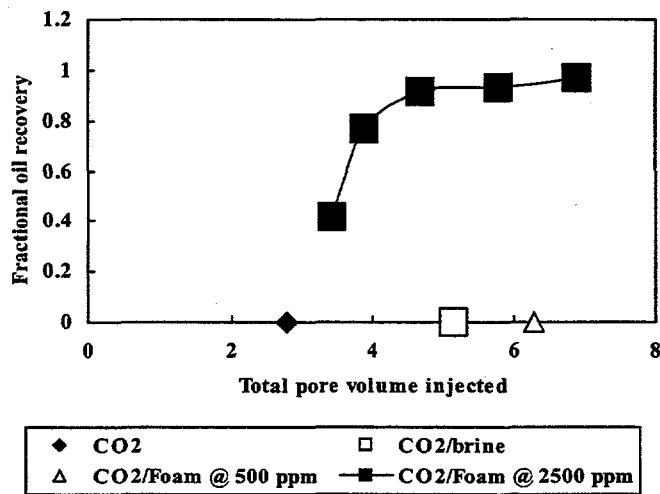

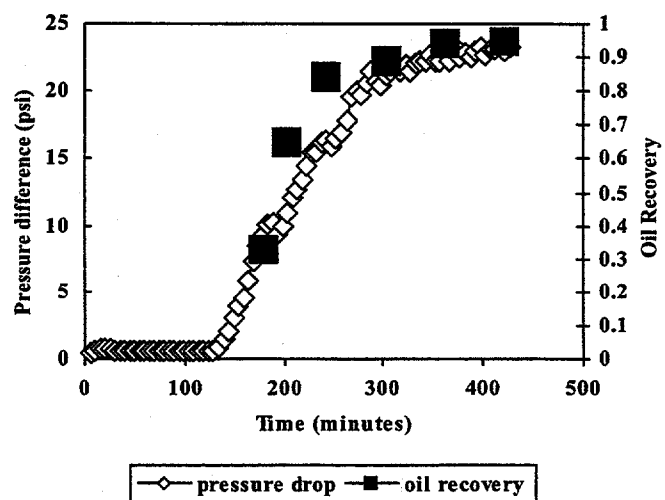Figure 2. Oil recovery through the low permeability (annulus) region.

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Figure 3. Pressure drop profile and oil recovery curve for high permeability region.
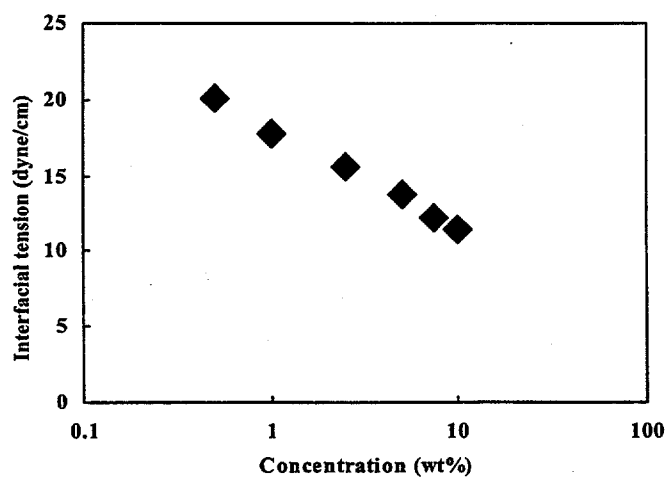

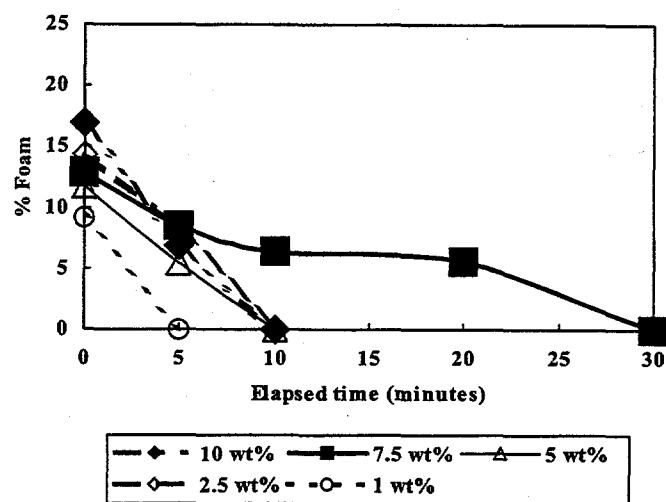Figure 4. IFTs between dense CO_2 and lignosulfonate.
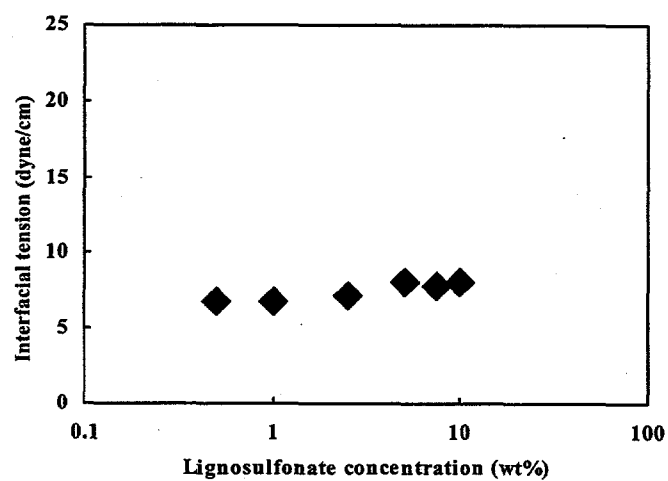
Figure 5. Decay of CO_2 foam with lignosulfonate.

Figure 6. IFTs between dense CO_2 and mixture of lignosulfonate and surfactant CD1045.
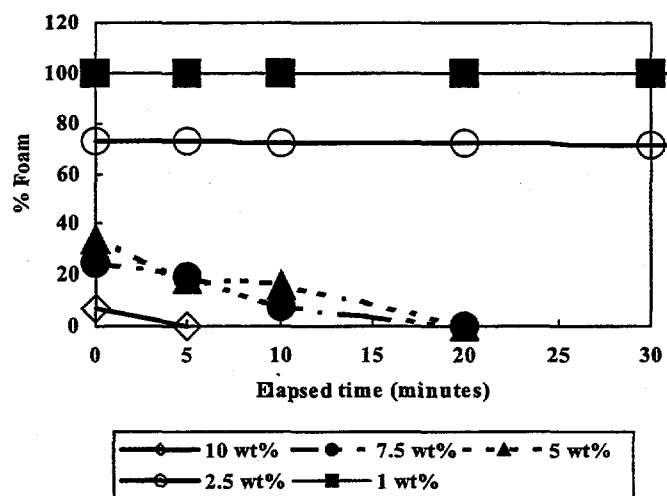
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Figure 7. Decay of CO_2 foam with mixture of lignosulfonate and 0.05 wt% CD1045.